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(54) Title: UNSATURATED ETHYLENE POLYMERS (57) Abstract Ethylene alpha, internal nonconjugated diene unsaturated copolymers and higher interpolymers having structural characteristics that provide improved physical properties and processability. The ethylene polymers of the invention have narrow molecular weight distribution and/or narrow composition distribution and/or a low cluster index. Ethylene/1,4-hexadiene and ethylene/vinyl cyclohexene polymers have residual unsaturation for subsequent modifications and for applications with improved toughness, printability, melt processability, and other advantageous characteristics.		

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UNSATURATED ETHYLENE POLYMERS1 BACKGROUND OF THE INVENTION

2 This invention relates to unsaturated ethylene polymers in
3 general and in particular to such polymers having residual
4 unsaturation, and formed by the polymerization of ethylene and an
5 alpha, internal nonconjugated diene (diolefin) comonomer.
6 Optionally, other monomers are also incorporated in the polyethylene
7 structure.

8 Polymers consisting primarily of ethylene monomer are widely
9 recognized materials for a great variety of uses in many fields.
10 Certain other polymers have disadvantages for some applications
11 because of the physical properties associated with the polymer
12 structure, whether from the incorporation of a comonomer or from the
13 method of polymerization of the polymer. Most homopolymers and
14 copolymers of alpha-olefins are widely used because of their
15 inexpensive nature and excellent physical properties including
16 transparency, moldability, chemical resistance, and other aspects.
17 However, such polymers generally do not have widespread suitability
18 for other substrates, surfaces, and materials due to their non-polar
19 structure. Accordingly, most such homopolymers, copolymers, and
20 higher interpolymers are not generally suitable for coatings,
21 printing, and antistatic applications. Various methods and
22 treatments have been devised to overcome the general shortcoming of
23 such polymers. These include treating the polymers with oxidizing
24 agents, degrading agents, and the like, but such measures have not
25 always proven satisfactory for all applications.

26 The present invention is related to ethylene homopolymers,
27 copolymers, terpolymers, and higher interpolymers of ethylene and
28 other copolymerizable comonomers which have alpha, internal
29 nonconjugated unsaturation. Such polymers always include a comonomer
30 moiety which provides unsaturation in the polymer, the unsaturation
31 being for subsequent modification or use in the various applications
32 for which the ethylene polymers are not otherwise suitable. Polymers
33 of ethylene are needed which not only incorporate residual
34 unsaturation but also have outstanding physical properties above
35 those commonly found in the predecessors of the present invention.

1 Ethylene and other alpha-olefins are traditionally polymerized or
2 copolymerized in the presence of catalytic complexes formed from
3 mixtures of transition metal compounds and aluminum alkyls. Such
4 complexes necessarily produce polymers and interpolymers which have
5 physical properties depending on the catalyst and method of
6 polymerization.

7 Prior art polymers have suffered from one or more
8 difficulties affecting their physical properties, especially for the
9 residual unsaturation polymers to which the present invention is
10 related since these polymers may not often be modified or degraded
11 without affecting the residual unsaturation content. The
12 difficulties include broadened molecular weight distributions,
13 broadened composition distribution of comonomer, and inefficient
14 distribution or dispersion of the comonomer along the polyethylene
15 chain of the copolymer. Of course, it is recognized that the
16 polymers of the invention have residual unsaturation along the side
17 chains substituted on the main polyethylene chain of the invention.

18 Broadened molecular weight distribution of a polymer
19 strongly influences its melt flow properties and such polymers tend
20 to have a high concentration of high molecular weight molecules
21 making them subject to orientation. As a result, such resins produce
22 strongly anisotropic physical properties in the machine transverse
23 direction of a fabrication process and such properties are
24 detrimental to a number of end use applications.

25 Broad molecular weight distribution resins also frequently
26 contain a significant portion of quite low molecular weight
27 material. These molecules almost invariably contain high
28 concentrations of comonomer and therefore tend to be amorphous or of
29 a low degree of crystallinity. Consequently, these materials exude
30 to the surface of fabricated parts causing tackiness where not
31 desired and/or interfere with other additives in the polymer designed
32 according to the particular application. An example of this is the
33 surface active property associated with slip agents in blown or cast
34 film.

35 Most prior art copolymers tend to have a very broad
36 composition distribution of comonomer, i.e., the distribution of
37 comonomer among the polymer molecules being nonuniform, some

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1 molecules having a relatively high concentration of comonomer while
2 others have a relatively low concentration of comonomer. This
3 structural property of the prior art polymers allows that portion
4 with low comonomer content to have a high melting point and vice
5 versa leading to a broad melting range for the entire polymer
6 composition. Of course the presence of a high melting component is
7 disadvantageous for many applications where softness is desired and
8 may lead to undesired stiffness. On the other hand, the presence of
9 high comonomer content materials of low melting point frequently
10 results in a high quantity of extractables.

11 Prior art materials are generally characterized by
12 relatively inefficient use of comonomer moieties along the
13 polyethylene chains. The distribution of the comonomer along the
14 chain is very important in determining the efficiency of use of the
15 comonomer and the resulting properties of the polymer, especially
16 with respect to crystallizability of the polymer. Such prior art
17 polymers tend to have a high degree of clustering of the comonomer
18 moieties along the polyethylene chain. That is, the comonomer units
19 are adjacent or nonisolated along the chain resulting in inefficient
20 use of the comonomer since only a single polyethylene chain
21 interruption results when several comonomer units are contiguous.
22 This has extremely important implications in the total amount of
23 comonomer required to achieve the desired crystallinity. Also, it is
24 often disadvantageous to include unneeded portions of comonomer,
25 especially when dealing with less available and more expensive diene
26 comonomers. Frequently, the requirement to use a higher portion of
27 comonomer also tends to force the comonomer into low molecular
28 weight, high comonomer content ends of the molecular weight
29 distribution. Accordingly, improved unsaturated ethylene copolymers,
30 terpolymers, and interpolymers in the entire range of amorphous to
31 highly crystalline polymers is needed.

32 BRIEF DESCRIPTION OF THE DRAWINGS

33 Figure 1 is a graphic and verbal depiction of the concept of
34 cluster index;

35 Figure 2 is a plot of cluster index against mole percent
36 comonomer for several commercial resins and the unsaturated resin of
37 the invention;

1 Figure 3 is an overlay of a plot of the molecular weight
2 distribution of resin of the invention over that for commercial resin
3 3, plotted against weight percent comonomer content;

4 Figure 4 is a series of plots of comonomer distribution in weight
5 percent versus elution temperature for resin of the invention and
6 several commercial resins;

7 Figure 5 is a plot evidencing the correlation of elution
8 temperature and polymer composition in branches/1000 carbon atoms
9 (mole percent comonomer);

10 Figure 6 is a plot for comparison to Figure 6A, showing the
11 relative breadth of melting point for some commercial polymers;

12 Figure 6A is a plot of the melting point by DSC for three
13 copolymers of the invention (Examples 1- 2A).

14 SUMMARY OF THE INVENTION

15 The present invention is directed to providing polymers of
16 ethylene and at least one comonomer wherein the at least one
17 comonomer is an alpha, internal nonconjugated diolefin and wherein
18 the polymer has excellent physical properties resulting from the
19 structure of the polymer and also has residual unsaturation. The
20 polymers of the invention generally comprise at least about 50
21 percent ethylene and the remainder alpha, internal nonconjugated
22 diolefin and optionally other polymerizable comonomer content. When
23 used herein, the term copolymer is intended to include terpolymers
24 and higher interpolymers of ethylene as well as the simple copolymer
25 of ethylene with a single diolefin or mixture of such alpha, internal
26 nonconjugated diolefins. Therefore, the term copolymer includes
27 terpolymers and interpolymers when referring to the polymers of the
28 present invention.

29 The polymers of the present invention may have a broad range
30 of densities and, therefore, applications for the particular type of
31 copolymer. In addition, the residual unsaturation of the copolymer
32 may vary quite widely by design according to the invention so as to
33 provide a copolymer of particular suitability for certain
34 applications. The polymers may be liquid or solid.

35 DESCRIPTION OF THE PREFERRED EMBODIMENTS

36 A copolymer composition from the polymerization of ethylene
37 and at least one polymerizable comonomer comprising an alpha,

1 internal nonconjugated diene, said copolymer having a composition
2 distribution wherein at least about 55 weight percent, preferably
3 about 65 weight percent, more preferably about 70 weight percent of
4 the copolymer molecules have a comonomer content within about 50
5 percent of the median comonomer content in mole percent of said
6 copolymer composition.

7 By way of explanation, a copolymer having a median (equal
8 amount greater and less than) comonomer content of 2.0 mole percent
9 would have 55 weight percent, preferably 65, more preferably 70
10 weight percent of its composition with a comonomer content of 1.0 to
11 3.0 mole percent.

12 Another preferred embodiment of the present invention is a
13 copolymer composition from the polymerization of ethylene and at
14 least one polymerizable comonomer comprising an alpha, internal
15 nonconjugated diene, said copolymer having a molecular weight
16 distribution (Mw/Mn) of about 3.0 or less, preferably 2.5 or less,
17 preferably about 2.0.

18 Another preferred embodiment of the present invention is a
19 copolymer composition from the polymerization of ethylene and at
20 least one comonomer comprising an alpha, internal nonconjugated
21 diene, said copolymer composition having incorporated in its
22 structure at least 3 mole percent preferably 5 mole percent, more
23 preferably 10 mole percent of units of said at least one comonomer,
24 said copolymer composition having a cluster index of about 9 or less,
25 preferably between 5 and 0.

26 The ethylene copolymers of the invention have improved
27 properties resulting especially from the more efficient use of diene
28 comonomer in controlling the crystallizability of the polymer. That
29 is, the efficient use of the diene comonomer comprises an improved
30 isolation of the comonomer molecules along the polyethylene chain as
31 not previously achieved for ethylene copolymers having residual
32 unsaturation. Accordingly, the polymers of the present invention not
33 only have especially good application for those uses previously
34 employing residual unsaturation polymers, but also have excellent
35 overall physical properties marking a significant improvement over
36 those materials previously available. The improved properties of the
37 invention result from the isolated dispersion of the diene comonomer

1 and other comonomers along the sequence of the polymer molecule of
2 the invention.

3 Another preferred embodiment copolymer of the present
4 invention has a distribution wherein more than 55 weight percent of
5 the copolymer molecules are within 50 percent of the median comonomer
6 content in the mole percent, said copolymer being formed by
7 polymerization in the presence of a catalyst system comprising a
8 metallocene of a metal of Group IVB, VB, and VIB of the Periodic
9 Table and an alumoxane or reaction product thereof.

10 The unsaturated copolymer products of the present invention
11 comprise batchwise or continuously produced bulk polymer compositions
12 having the properties and characteristics described herein. No such
13 compositions have heretofore been discovered. That is, the
14 entire/unmodified polymerization product has the advantageous
15 properties.

16 The unsaturated copolymer compositions of the invention may
17 be prepared from the polymerization of ethylene and at least one
18 comonomer. The at least one comonomer comprises, that is always
19 includes some (or all) of the alpha, internal nonconjugated diene.

20 The alpha, internal nonconjugated diene comonomers of the
21 invention may be linear or cyclic, branched or unbranched, short or
22 long chained.

23 The diene comonomers incorporated in the unsaturated
24 polymers of the invention may be in small or large quantity relative
25 to the amount of ethylene in the polymer. In one embodiment of the
26 invention, the polymers of the invention contain at least a minimum
27 of about 3 mole percent total comonomer based on the moles of
28 ethylene and comonomers, so as to provide wide dispersion of the
29 comonomers in the polymer product composition. This generally limits
30 the density to a number below 0.930 g/cc, preferably below 0.920 g/cc
31 depending on the copolymers chosen and the method of incorporation.
32 Thus, where only a two component polymer composition is formed from
33 ethylene and the alpha, internal nonconjugated diene, at least about
34 3 mole percent diene units and no more than about 97 mole percent
35 ethylene units are present. For terpolymers and higher interpolymers
36 of the invention, only about 0.01 mole percent or more, preferably
37 about 0.1 mole percent or more, more preferably 1 mole percent or

1 more of the diene need be incorporated so long as the total
2 incorporation of comonomers (diene and other[s]) is at least about 3
3 mole percent for this embodiment.

4 Despite incorporation of at least about 3 mole percent
5 comonomer units in one embodiment of the polymer compositions of the
6 invention the polymers nevertheless have a low cluster index and
7 preferably other characteristics described herein. The total
8 comonomer content of the polymers of the invention may be the
9 predominant portion of the polymer. Preferably, especially for solid
10 unsaturated polymers, the ethylene units are the predominant
11 component on a molar basis.

12 In one preferred embodiment of the present invention the
13 polymers of the invention have improved properties attributable to
14 the more uniform content of diene and other comonomer among the
15 polymer molecules.

16 In contrast to the prior art polymers, the copolymers,
17 terpolymers, and other interpolymers of the present invention have
18 residual unsaturation and exhibit very little clustering of the
19 comonomer molecules along the polyethylene chain both with respect to
20 the diene comonomer and any other polymerizable comonomer formed in
21 the polyethylene chain. As a result, the use of comonomer in forming
22 the copolymers of the invention is very efficient in controlling
23 crystallizability, wards against formation of high comonomer
24 content/low molecular weight ends, reduces cost, and improves
25 properties.

26 In a preferred embodiment of the present invention, the
27 copolymers of the invention have very narrow composition distribution
28 of comonomer. That is, the copolymers have much more uniform
29 distribution of comonomer among the molecules thereby largely
30 avoiding the problem presented by broad composition distribution
31 resins.

32 In another preferred delineation of the invention, the
33 copolymers of the invention have improved properties resulting from
34 the more consistent size of polymer molecules not achieved in the
35 prior art. This aspect of the more preferred embodiment is generally
36 referred to as the improved molecular weight distribution or ratio of
37 the weight average molecular weight to number average molecular

1 weight of the polymer material.

2 Also in this preferred embodiment of the present invention,
3 the copolymers of the invention exhibit relatively narrow molecular
4 weight distribution. That is, they have a relatively low ratio of
5 weight to number average molecular weight. In other words, the
6 concentration of very high molecular weight molecules and very low
7 molecular weight molecules is decreased over prior art unsaturated
8 polymers. The absence of the high molecular weight molecules reduces
9 the tendency for orientation in fabrication processes and increases
10 isotropic machine/transverse direction physical properties. The
11 absence of a low molecular weight molecules (low tail) in the
12 copolymers of the invention reduces the tendency to form tacky
13 surfaces and otherwise interfere with surface active agents in
14 certain applications of the copolymers of the present invention.

15 Unsaturated polymers of the prior art do not have the
16 structure and corresponding properties of the polymers of the
17 invention. That is, they lack the low cluster index for ethylene
18 copolymers (including terpolymers and higher interpolymers) having
19 therein at least about 3 mole percent, preferably 5 mole percent,
20 more preferably 10 mole percent comonomer units according to the
21 invention. The absence of such structure is generally reflected in
22 easily measured characteristics of the invention such as melting
23 point temperature and the like. The prior art unsaturated polymers
24 also generally lack narrow molecular weight distribution and narrow
25 comonomer distribution.

26 The polymers of the present invention are capable of being
27 fabricated into a wide variety of articles, as is known for
28 homopolymers of ethylene and copolymers of ethylene and higher
29 alpha-olefins. Furthermore, the polymers of the present invention
30 typically have residual unsaturation which permits their use in
31 additional applications where the residual unsaturation may be used
32 for bondability, printability, crosslinkability, and the like.

33 The unsaturated polymers of the invention may vary in
34 density across a broad scale from essentially amorphous materials to
35 highly crystalline materials. They may be liquids (such as for
36 certain rubbers and lubricants and waxes) or solids.

37 The molecular weight of the copolymers of the invention may

1 vary over a broad range. Preferably the polymers have a number
2 average molecular weight of about 500 or higher, preferably 1000 or
3 higher, more preferably about 10,000 or higher. Typically, materials
4 used for elastomers applications are either copolymers or terpolymers
5 (often with propylene monomer) in the density range of about
6 0.86-0.87 g/cc. Typically, these polymers contain 30 weight percent
7 or more of the comonomers and the balance ethylene. Frequently, the
8 elastomers of the unsaturated polymers of the invention will have as
9 much as 48 weight percent of the comonomer present.

10 The unsaturated polymers of the present invention may also
11 include plastomers in the density range of about 0.87-0.900 g/cc and
12 containing from about 20-30 weight percent of comonomer. Also
13 available in the unsaturated polymers of the invention are the very
14 low density polyethylene materials of density range 0.900-0.915 g/cc
15 and having from about 10-20 weight percent comonomer present.

16 The unsaturated polymers of the invention may be formed as a
17 linear low density polyethylene type polymer in the density range of
18 about 0.915 g/cc to about 0.940 g/cc and containing from about 5-10
19 weight percent of the comonomers. The unsaturated polymers of the
20 invention may also be used in the form of high density polyethylene
21 having a density of about 0.940 g/cc and above and containing up to
22 about 5 weight percent comonomers. The unsaturated polymers of the
23 invention may also form amorphous materials below a density of 0.86
24 g/cc including tackifier resins.

25 The unsaturated polymers of the present invention have
26 particularly advantageous properties because of their narrow
27 molecular weight distribution, narrow compositional distribution, and
28 their chain configuration having isolated comonomer units.

29 Sequence distributions, or the distribution of comonomer
30 units along a polymer chain, in, e.g., linear low density
31 polyethylenes is a factor affecting the cost of the polymer because
32 it affects the amount of comonomer required to achieve a desired
33 polymer density. If comonomer is efficiently incorporated, i.e.,
34 with little clustering of comonomer units, in a linear low density
35 polyethylene, less comonomer is required to depress the density.
36 Thus, the number of comonomer runs in a copolymer chain and the
37 length of each run is significant in the structure of the

1 polyethylene molecules and affects the physical properties of the
2 polymer. The polymers of the present invention are marked by a
3 relatively high number of single units of comonomer in the polymer
4 chain relative to the number of units containing more than a single
5 comonomer molecule in comparison to unsaturated polymers of the prior
6 art.

7 The unsaturated ethylene polymers of the invention are
8 hereinafter described by their "cluster index". This index reflects
9 the degree to which the polymers of the invention have individual
10 comonomer units dispersed along the polyethylene chain, preferably in
11 favoring isolation of individual units over groups of two or more
12 units. Given a minimum level of comonomer, the unsaturated ethylene
13 polymers of the present invention are especially noted for their
14 efficient use of comonomer molecules by having more isolated
15 comonomer molecules along the polyethylene chain and fewer clusters
16 of molecules of the comonomer in the polyethylene chain. That is,
17 the unsaturated polymers of the present invention tend to deviate
18 from random comonomer distribution in the direction of fewer
19 contiguous comonomer sequences. Thus, the cluster index permits a
20 quantitative evaluation of the deviation from a random distribution
21 of comonomer in the polymer chain.

22 In the cluster index description given herein, there are two
23 reference points. The reference point 0 describes a polymer which
24 has only isolated comonomer insertions without any contiguous
25 comonomer units in a cluster; of course this describes pure
26 homopolymers also. The second reference point is the number 10
27 describing an ethylene copolymer having comonomer distribution that
28 is exactly random (Bernoullian) and thus containing a predictable
29 amount of contiguous comonomer units. Any polymer having a cluster
30 index value greater than 10 contains proportionally more contiguous
31 comonomer sequences than predicted by the random distribution. Any
32 polymer having a cluster index value between 0 and 10 is indicated to
33 have fewer contiguous sequences than a random distribution polymer
34 (given a minimum of comonomer). These values are typically
35 associated with the method of producing the polymer including the
36 catalyst used and conditions of polymerization.

37 The cluster index comparisons are best made for polymers

1 having comparable comonomer mole contents or densities. The
 2 measurement of the clustering of the comonomer along the polyethylene
 3 chain in a given polymer may be determined by a study using carbon 13
 4 nuclear magnetic resonance spectroscopy (C^{13} NMR). Using this tool
 5 for evaluation, the cluster index may be given as follows:

$$6 \quad \text{Cluster index} = 10 [(X) - (EXE)]/[2(X)^2 - (X)^3]$$

7 where (X) is the mole % of total comonomer molecules in the
 8 copolymer and (EXE) is the mole fraction of the triad segment of
 9 3 monomer units containing ethylene-comonomer-ethylene. These
 10 concentrations are easily measured using C^{13} NMR.

11 The basis for the cluster index is further explained and
 12 exemplified below by the following discussion and in reference to
 13 drawing Figure 1.

14 Referring now to drawing Figure 1 the cluster index may be
 15 derived as follows, using the reference point 10 as random clustering
 16 expected in a polymerization and the reference point 0 as that point
 17 for no clustering in a polymer (no units of more than one comonomer
 18 molecule contiguous). Accordingly,

$$19 \quad \text{Cluster index} = 10 - 10 \times \frac{[(EXE)_{\text{observed}} - (EXE)_{\text{random}}]}{[(X) - (EXE)_{\text{random}}]}$$

22 where "X" is the mole % comonomer in the ethylene copolymer and
 23 EXE is the corresponding triad configuration of a single
 24 comonomer molecule contiguous to two ethylene molecules (units).

25 The term $(EXE)_{\text{random}}$ serves as a reference point and its
 26 value can be calculated from any suitable statistical model. In this
 27 case the Bernoullian model was chosen. For the Bernoullian model

$$28 \quad (EXE)_{\text{random}} = [1 - X]^2[X].$$

29 Thus, substituting this value of $(EXE)_{\text{random}}$ in the formula for
 30 cluster index above gives:

$$\text{Cluster index} = 10 [(X) - (EXE)_{\text{observed}}] / [2(X)^2 - (X)^3]$$

Accordingly, it can be readily seen from drawing Figure 1 that those polymers having more comonomer clustering than a random distribution appear to the left of the reference point 10 and those having less comonomer clustering than a random distribution appear between 0 and 10.

In Figure 2, polymers are plotted according to their cluster index as described for Figure 1 and using the vertical axis to plot mole percent of comonomer of the polymer samples. It is readily apparent from drawing Figure 2 that those polymers of the invention have a reduced cluster index (for a given density) over polymers of the prior art such as those commercial polymers plotted and appearing near or to the left of reference point 10 (random clustering). The technique of using the C^{13} NMR to obtain the information for cluster index is known to the skilled artisan.

Also shown for comparison in Figure 2 is the cluster index of Dowlex 2088 octene LLDPE copolymer (Resin 9), Dowlex 2517 octene LLDPE copolymer (Resin 10), and Union Carbide 7099 hexene LLDPE copolymer (Resin 11).

The cluster index improvement in the polymers of the invention versus polymers of the prior art is detectable at 3 mole percent comonomer content, readily discernable at 5 mole percent, and remarkable at about 10 mole percent or higher.

The above described cluster index may be considered to be of the first order or based on the total number of comonomer units less the isolated (EXE) comonomer units. A higher order cluster index can also be measured and calculated as based primarily on the occurrence of dimer segments (EXX) or (XXE) as observed. This measurement is somewhat more discriminating at low comonomer mole percents (about 3). Thus, an EXX index may in like fashion be calculated as:

$$\text{EXX index} = 10 - 10 \times \frac{[(EXX)_{\text{observed}} - (EXX)_{\text{Bernoullian}}]}{(EXX)_{\text{Bernoullian}}}$$

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1 Since $(EXX)_{\text{Bernoullian}} = 2[E][X]^2$ and the (EXX) observed is
2 based on both (EXX) and (XXE) units, readily measured by C^{13}
3 NMR, the EXX index is readily achieved. For such index a totally
4 random polymer is measured as 10, a totally dimerless polymer is
5 0 (no contiguous XX), and a polymer increasingly deficient in
6 solitary units (EXE) will approach 20.

7 The EXX index is a second measure of polymer structure based
8 directly on dimers and higher orders of contiguous X (EXX and XXE)
9 observed; it may be used independently or together with the cluster
10 index (EXE) to distinguish polymers.

11 The EXX index for commercial resins 3, 5, and 6 in the Table
12 herein are 7.3, 12.4, and 15.0. Compare the terpolymer resin of
13 Example 2 of the invention which at 3.9 mole percent comonomer has an
14 EXX index of only 8.2.

15 The unsaturated ethylene polymers of the present invention
16 are preferably marked by a relatively narrow molecular weight
17 distribution in comparison to prior art polymers. The molecular
18 weights and molecular weight distributions were determined using
19 Waters 150C Gel Permeation Chromatographic Instruments. These
20 instruments were equipped with refractive index detectors operated at
21 145°C and at a solvent flow rate of 1 milliliter per minute. The
22 solvent used was ultra-high purity grade 1,2,4-trichlorobenzene
23 obtained from Burdick and Jackson Company. Prior to use, the solvent
24 was filtered through a 0.5 micron filter and stabilized with 120 ppm
25 BHT. Three Waters styragel columns were used with nominal porosities
26 of 500, 10,000, and 1,000,000 angstroms. Each polymer sample was
27 dissolved in trichlorobenzene solvent at 145°C to a concentration
28 level of about 0.1 weight percent and thereafter filtered through a
29 0.5 micron porous metal filter. About 300 microliters of this
30 solution was then injected into the gel permeation chromatograph.
31 Analysis time was typically 45 minutes. Calibration of the
32 instrument for molecular weight determination was accomplished with
33 the use of narrow molecular weight distribution polystyrene standards
34 obtained from Toyo Soda Manufacturing Company. Sixteen of the
35 standards were used ranging in molecular weight from 526 - $5.2 \times$
36 10^6 . Molecular weight distributions of these standards were listed
37 at 1.0-1.15 as measured by the ratio of weight average molecular

1 weight to number average molecular weight. These polystyrene
2 molecular weight data were then converted to a polyethylene basis
3 with the use of the Mark-Houwink equation and the use of the
4 following constants:

5 for polyethylene $K = 5.17 \times 10^{-4}$, $a = 0.70$

6 for polystyrene $K = 2.78 \times 10^{-4}$, $a = 0.70$.

7 Each sample was run twice and the calculated results average to yield
8 the molecular weight information reported. The molecular weight
9 distribution of the resin of Example 1 below was plotted for
10 comparison on the same plot with that for Exxon LL3001 linear low
11 density polyethylene resin mole percent comonomer on a scale of the
12 log of molecular weight versus weight percent of the polymer in the
13 molecular weight range. As can be seen from drawing Figure 3 the
14 unsaturated polymer of the invention has a strictly narrower
15 molecular weight distribution than the commercially available linear
16 low density polyethylene.

17 The unsaturated polymers of the present invention preferably
18 also have a narrow distribution of comonomer amongst molecules of the
19 polymer in comparison to prior art polymers. For comparison, drawing
20 Figure 4 reflects the narrow distribution of the unsaturated polymer
21 of Example 1 in comparison to the relatively broad comonomer
22 distribution polymers of the prior art. In Figure 4 the weight
23 percent of copolymer (having a given comonomer content) is plotted
24 against an elution temperature which directly reflects comonomer
25 content. A better understanding of this preferred embodiment of the
26 polymers of the present invention will be had by a review of Figure 4
27 and the following discussion.

28 Crystalline copolymers may be fractionated by comonomer
29 content over a temperature range from 0-120°C in tetrachloroethylene
30 solvent. The compositions of the fractions of the copolymer are
31 determined and a solution temperature versus composition calibration
32 curve has been constructed based on the data obtained. Using this
33 calibration curve, the temperature scale of the solubility
34 distribution curve can be converted to a composition scale and a
35 composition distribution curve is thus obtained as in drawing Figure
36 4.

37 A machine has been assembled to automatically determine the

1 solubility distribution curve of a crystalline copolymer. In the
2 measuring instrument, a steel column is packed with small mesh glass
3 beads and immersed in an oil bath whose temperature can be programmed
4 over a temperature range from about 0°C-150°C. The
5 tetrachloroethylene solvent may be prevented from boiling by
6 operating the instrument at about 3 atmospheres pressure under an
7 automatic regulator. A weighed amount of sample, usually about 1.6
8 grams, is placed in a sample preparation chamber, sealed, and
9 repeatedly evacuated and filled with argon. A metered volume of
10 solvent is then pumped into the sample preparation chamber where it
11 is stirred and heated to obtain a solution of about 1 percent
12 concentration. A metered volume of this solution, usually about
13 100 cc is then pumped into the packed column which has been
14 thermostated at a high temperature of usually at least about 120°C.

15 The polymer solution sample is subsequently crystallized by
16 cooling the polymer in the column to 0°C at a programmed rate of 5°C
17 per hour. The column was then maintained at 0°C for at least an
18 hour. Thereafter, the elution stage of the determination is started
19 by pumping pure solvent through the column at a rate of 6 cc per
20 minute. Effluent from the column passes through the reheater where
21 it is heated to 120°C before passing through an IR detector used to
22 measure the absorbance of the effluent stream. The infrared
23 absorbents of the polymer carbon hydrogen stretching bands at about
24 2960 centimeter⁻¹ serves as a continuous measure of the relative
25 concentration of polymer in the effluent. After passing through the
26 infrared detector the temperature of the effluent is reduced to about
27 110°C and the pressure is reduced to 1 atmosphere before passing the
28 stream into an automatic fraction collector. In the elution stage,
29 the pure solvent is pumped through the column set at 0°C for one
30 hour. This serves to flush polymer that has not crystallized during
31 the crystallization stage out of the column so that the percent of
32 uncrystallized polymer can be determined from the infrared trace.
33 The temperature is then programmed upward at 10°C per hour to 100°C
34 and at 20°C per hour from 100°C to 120°C.

35 The compositions of fractions obtained from the various
36 polymers were determined by infrared spectroscopy. The IR
37 compositions are obtained from the intensity of the 1378(cm)⁻¹

1 methyl band, the thickness of the sample, and a calibration curve
2 based on samples whose compositions were determined independently by
3 C^{13} NMR. No corrections for polymer end groups was made in
4 obtaining compositions from infrared data.

5 Figure 5 is a plot of the elution temperature versus the
6 comonomer content in mole percent comonomer (branches per 1000 carbon
7 atoms) for the fractions of the sample. The curve "A" has been drawn
8 through the points. Thus, curve A may be used as a correlation
9 between elution temperature and composition of the polymer for
10 temperatures greater than 0°C. The calibration curve is most
11 accurate for fractions with number average molecular weights, M_n
12 $\geq 10,000$ as determined by size exclusion chromatography.

13 As seen in drawing Figure 4, samples of polymers tend to
14 have a peak at about 0°C elution temperature. This small peak
15 represents the fraction of total polymer that is not crystallizable
16 at the lowest temperature of the experiment (about 0°C).

17 In summary, the device and procedure described provide a
18 plot of relative weight percent of polymer versus elution temperature
19 which in turn may be correlated to composition and mole percent
20 comonomer (branches per 1000 carbon atoms) in the polymer chain.
21 Accordingly, drawing Figure 4 is an effective comparison of the
22 comonomer distribution of the unsaturated polymers of the invention
23 to that for certain commercial polymers. As can readily be seen, the
24 composition distribution of the polymer of the invention example is
25 quite narrow in comparison.

26 The alpha internal nonconjugated dienes which form units of
27 the copolymers (including terpolymers and higher interpolymers) of
28 the invention include a variety of such diolefins exemplified by but
29 not limited to the following:

30 1,4-hexadiene; 1,4-heptadiene; 1,5-heptadiene;
31 1,4-octadiene; 1,5-octadiene; 1,6-octadiene; 4-methyl-1,4-hexadiene,
32 5-methyl-1,4-hexadiene, 4-ethyl-1,4-hexadiene,
33 5-methyl-1,4-heptadiene; 5-ethyl-1,6-octadiene; 3-vinyl cyclohexene;
34 4-vinyl cyclohexene; 3-vinyl cyclopentene; cis and trans
35 1,5,9-decatriene; 5-vinyl norbornene; 1,4-dodecadiene.

36 Comonomers other than the dienes of the invention include
37 polymerizable comonomers such as acids, esters, other olefins, and

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1 the like. Suitable olefins include the alpha olefins such as
2 propylene, butene, hexene, octene, 4-methyl-pentene-1, and others.

3 According to the invention, the alpha-olefin content of the
4 unsaturated ethylene polymers (copolymers) of the invention is less
5 than 15 weight percent, preferably less than 10 weight percent.

6 In forming the polymers of the present invention it may be
7 necessary to purify, or isolate the diene and other, optional
8 comonomers of the invention in order to obtain incorporation thereof
9 during polymerization. One such recommended technique is passing the
10 comonomer, especially the diene, over alumina to remove extraneous
11 materials.

12 Figures 5 and 6A show the melting point by differential
13 scanning calorimetry results for the resins of the invention in
14 comparison to some commercial resins. Melting point distributions
15 were determined using a Perkin Elmer DSC-7 operated in the following
16 fashion: About 5-6 mg of sample was heated to 160°C and held at that
17 temperature for 5 minutes. The sample was then cooled at 10°C per
18 minute to a temperature of 0°C and reheated at 10°C per minute. The
19 melting distributions reported here were collected during this
20 reheating at 10°C per minute.

21 Concentrations of unsaturation in ethylene based polymers
22 was determined by comparisons of IR spectra of brominated versus
23 original polymer specimens utilizing the following bands:

24 vinylene - 965 cm^{-1}
25 vinyl - 909 cm^{-1}
26 vinylidene - 888 cm^{-1}

27 A better understanding of the invention will be had by a
28 review of the above discussion in conjunction with the drawing
29 Figures and the Examples given below. The best mode of the invention
30 presently known is described herein.

31 The unsaturated polymers of the present invention are those
32 having the narrow cluster index and preferably having the additional
33 described structure of molecular weight distribution and comonomer
34 distribution as well as properties herein described. Such polymers
35 may be prepared by any of the known techniques of polymerization
36 including solution, high pressure, and gas-phase polymerization
37 processes.

38 The polymers of the invention may be formed by use of
39 catalyst systems of the metallocene type. That is,

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1 cyclopentadienylide catalyst systems using a metallocene complex in
2 conjunction with an alumoxane cocatalyst or reaction product thereof
3 are suitable for preparing polymers of the invention. The
4 metallocene catalyst may be represented by the general formula
5 $(Cp)_m MR'_n R'_p$ wherein Cp is a substituted or unsubstituted
6 cyclopentadienyl ring; M is a Group IVB, VB, or VIB transition metal;
7 R and R' are independently selected halogen, hydrocarbyl group, or
8 hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p =
9 0-3; and the sum of m + n + p equals the oxidation state of M.
10 Various forms of the catalyst system of the metallocene type may be
11 used for polymerization to achieve polymers of the present invention
12 including those of the homogeneous or the heterogeneous, supported
13 catalyst type wherein the catalyst and alumoxane cocatalyst are
14 together supported or reacted together onto an inert support for
15 polymerization by gas-phase, high pressure, or solution
16 polymerization.

17 The cyclopentadienyls of the catalyst may be unsubstituted
18 or substituted with hydrogen or hydrocarbyl radicals. The
19 hydrocarbyl radicals may include alkyl, alkenyl, aryl, alkylaryl,
20 arylalkyl, and like radicals containing from about 1-20 carbon atoms
21 or 2 carbon atoms joined together to form a C_4-C_6 ring.
22 Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, butyl,
23 amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl,
24 2-ethylhexyl, phenyl and the like. Exemplary halogen substituents
25 include chlorine, bromine, fluorine and iodine and of these halogen
26 atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are
27 methoxy, ethoxy, propoxy, butoxy, amyloxy and the like.
28 Illustrative, but non-limiting examples of the metallocene catalyst
29 useful in preparing the polymers of the present invention include
30 bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium
31 diphenyl, bis(cyclopentadienyl)zirconium dimethyl,
32 bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium
33 dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl,
34 bis(cyclopentadienyl)zirconium di-neopentyl,
35 bis(cyclopentadienyl)titanium dibenzyl,
36 bis(cyclopentadienyl)zirconium dibenzyl,
37 bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes
38 such as bis(cyclopentadienyl)titanium methyl chloride,

- 1 bis(cyclopentadienyl)titanium ethyl chloride,
- 2 bis(cyclopentadienyl)titanium phenyl chloride,
- 3 bis(cyclopentadienyl)zirconium methyl chloride,
- 4 bis(cyclopentadienyl)zirconium ethyl chloride,
- 5 bis(cyclopentadienyl)zirconium phenyl chloride,
- 6 bis(cyclopentadienyl)titanium methyl bromide,
- 7 bis(cyclopentadienyl)methyl iodide, bis(cyclopentadienyl)titanium
- 8 ethyl bromide, bis(cyclopentadienyl)titanium ethyl iodide,
- 9 bis(cyclopentadienyl)titanium phenyl bromide,
- 10 bis(cyclopentadienyl)titanium phenyl iodide,
- 11 bis(cyclopentadienyl)zirconium methyl bromide,
- 12 bis(cyclopentadienyl)zirconium methyl iodide,
- 13 bis(cyclopentadienyl)zirconium ethyl bromide,
- 14 bis(cyclopentadienyl)zirconium ethyl iodide,
- 15 bis(cyclopentadienyl)zirconium phenyl bromide,
- 16 bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl
- 17 metallocenes such as cyclopentadienyltitanium trimethyl,
- 18 cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium
- 19 trineopentyl, cyclopentadienylzirconium trimethyl,
- 20 cyclopentadienylhafnium triphenyl, cyclopentadienylhafnium
- 21 trineopentyl, and cyclopentadienylhafnium trimethyl.
- 22 Other metallocenes which may be usefully employed to prepare
- 23 the polymers of the invention include the monocyclopentadienyls
- 24 titanocenes such as, pentamethylcyclopentadienyl titanium
- 25 trichloride, pentaethylcyclopentadienyl titanium trichloride;
- 26 bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene
- 27 represented by the formula bis(cyclopentadienyl)titanium=CH₂ and
- 28 derivatives of this reagent such as
- 29 bis(cyclopentadienyl)Ti=CH₂.Al(CH₃)₃, (Cp₂TiCH₂)₂,
- 30 Cp₂TiCH₂CH(CH₃)CH₂, Cp₂Ti-CHCH₂CH₂; substituted
- 31 bis(cyclopentadienyl)titanium (IV) compounds such as:
- 32 bis(indenyl)titanium diphenyl or dichloride,
- 33 bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl,
- 34 trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium
- 35 compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl
- 36 or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or
- 37 dichloride and other dihalide complexes; silicon, phosphine, amine or

1 carbon bridged cyclopentadiene complexes, such as dimethyl
2 silyldicyclopentadienyl titanium diphenyl or dichloride, methyl
3 phosphine dicyclopentadienyl titanium diphenyl or dichloride,
4 methylenedicyclopentadienyl titanium diphenyl or dichloride and other
5 dihalide complexes and the like.

6 Additional zirconocene catalysts useful according to the
7 present invention include bis(cyclopentadienyl)zirconium dimethyl,
8 bis(cyclopentadienyl)zirconium dichloride,
9 bis(cyclopentadienyl)zirconium methylchloride,
10 pentamethylcyclopentadienyl zirconium trichloride,
11 pentaethylcyclopentadienyl zirconium trichloride,
12 bis(pentamethylcyclopentadienyl)zirconium diphenyl, the alkyl
13 substituted cyclopentadienes, such as bis(ethyl
14 cyclopentadienyl)zirconium dimethyl,
15 bis(β -phenylpropylcyclopentadienyl)zirconium dimethyl,
16 bis(methylcyclopentadienyl)zirconium dimethyl,
17 bis(n-butyl-cyclopentadienyl)zirconium dimethyl,
18 bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl,
19 bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and
20 dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and
21 penta-alkyl cyclopentadienes, such as
22 bis(pentamethylcyclopentadienyl) zirconium di-methyl,
23 bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl and dihalide
24 complexes of the above; silicone, phosphorus, and carbon bridged
25 cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl
26 zirconium dimethyl or dihalide, and methylene dicyclopentadienyl
27 zirconium dimethyl or dihalide, and methylene dicyclopentadienyl
28 zirconium dimethyl or dihalide, carbenes represented by the formula
29 $\text{Cp}_2\text{Zr}=\text{CHP}(\text{C}_6\text{H}_5)_2\text{CH}_3$, and derivatives of these compounds
30 such as $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$.

31 Bis(cyclopentadienyl)hafnium dichloride,
32 bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium
33 dichloride and the like are illustrative of other metallocenes.

34 Various inorganic oxide supports may be used for supported
35 catalyst systems to prepare polymers of the present invention. The
36 polymerizations are generally carried in the temperature range of
37 about 0-160°C or even higher but this range is not meant to be

1 exclusive for preparing the polymers of the invention which may be
2 prepared by any technique resulting in the structure set forth.
3 Atmospheric, sub-atmospheric, or super-atmospheric pressure
4 conditions may exist for the polymerization using the metallocene
5 catalyst described above. It is generally preferred to use catalyst
6 compositions at a concentration so as to provide from about 1 ppm to
7 about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of
8 transition metal based on the weight of monomers in the
9 polymerization of the ethylene polymers.

10 A slurry polymerization process may generally use
11 sub-atmospheric or super-atmospheric pressures and temperatures in
12 the range of 40-110°C. In a slurry polymerization, a suspension of
13 solid, particulate polymer is formed in a liquid polymerization
14 medium to which ethylene and comonomers and often hydrogen along with
15 catalyst are added. The liquid employed in the polymerization medium
16 can be alkane or cycloalkane, or an aromatic hydrocarbon such as
17 toluene, ethylbenzene or xylene. The medium employed should be
18 liquid under the conditions of polymerization and relatively inert.
19 Preferably, hexane or toluene is employed.

20 In a modification, polymers of the present invention may be
21 formed by gas-phase polymerization. A gas-phase process utilizes
22 super-atmospheric pressure and temperatures in the range of about
23 50°-120°C. Gas-phase polymerization can be performed in a stirred or
24 fluidized bed of catalyst and product particles in a pressure vessel
25 adapted to permit the separation of product particles from unreacted
26 gases. Thermostated ethylene, comonomer (including diene), hydrogen
27 and an inert diluent gas such as nitrogen can be introduced or
28 recirculated so as to maintain the particles at a temperature of
29 50°-120°C. Triethylaluminum may be added as needed as a scavenger of
30 water, oxygen, and other adventitious impurities. Polymer product
31 can be withdrawn continuously or semi-continuously at a rate such as to
32 maintain a constant product inventory in the reactor. After
33 polymerization and deactivation of the catalyst, the product polymer
34 can be recovered by any suitable means. In commercial practice, the
35 polymer product can be recovered directly from the gas phase reactor,
36 freed of residual monomer with a nitrogen purge, and used without
37 further deactivation or catalyst removal. The polymer obtained can

1 be extruded into water and cut into pellets or other suitable
2 comminuted shapes. Pigments, antioxidants and other additives, as is
3 known in the art, may be added to the polymer.

4 The molecular weight of polymer product obtained in
5 accordance with this invention can vary over a wide range, as low as
6 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

7 For the production of polymer product having a narrow
8 molecular weight distribution, it is preferable to deposit only one
9 metallocene on to the inert porous support material and employ said
10 support metallocene together with the alumoxane as the polymerization
11 catalyst.

12 It is highly desirable to have for many applications, such
13 as extrusion and molding processes, polyethylenes which have a broad
14 molecular weight distribution of the unimodal and/or the multimodal
15 type. Such polyethylenes evidence excellent processability, i.e.
16 they can be processed at a faster throughput rate with lower energy
17 requirements and at the same time such polymers would evidence
18 reduced melt flow perturbations. Such polyethylenes can be obtained
19 by providing a catalyst component comprising at least two different
20 metallocenes, each having different propagation and termination rate
21 constants for ethylene polymerizations. Such rate constants are
22 readily determined by one of ordinary skill in the art.

23 The molar ratio of the metallocenes, such as, for example,
24 of a zirconocene to a titanocene in such catalysts, can vary over a
25 wide range, and in accordance with this invention, the only
26 limitation on the molar ratios is the breadth of the Mw distribution
27 or the degree of bimodality desired in the product polymer.
28 Desirably, the metallocene to metallocene molar ratio will be about
29 1:100 to about 100:1, and preferably 1:10 to about 10:1.

30 Examples

31 In the Examples following the alumoxane employed was
32 prepared by adding 76.5 grams ferrous sulfate heptahydrate in 4
33 equally spaced increments over a 2 hour period to a rapidly stirred 2
34 liter round-bottom flask containing 1 liter of a 13.1 weight percent
35 solution of trimethylaluminum (TMA) in toluene. The flask was
36 maintained at 50°C and under a nitrogen atmosphere. Methane produced
37 was continuously vented. Upon completion of the addition of ferrous

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1 sulfate heptahydrate, the flask was continuously stirred and
2 maintained at a temperature of 50°C for 6 hours. The reaction
3 mixture was cooled to room temperature and was allowed to settle.
4 The clear solution containing the alumoxane was separated by
5 decantation from the insoluble solids.

6 Molecular weights were determined on a Water's Associates
7 Model No. 150C GPC (Gel Permeation Chromatography). The measurements
8 were obtained by dissolving polymer samples in hot trichlorobenzene
9 and filtered. The GPC runs are performed at 145°C in
10 trichlorobenzene at 1.0 ml/min flow using styragel columns from
11 Perkin Elmer, Inc. 0.1 percent solutions (300 microliters of
12 trichlorobenzene solution) were injected and the samples were run in
13 duplicate. The integration parameters were obtained with a
14 Hewlett-Packard Data Module.

15 Example 1

16 A 1-liter stainless steel pressure vessel, equipped with an
17 incline blade stirrer, an external water jacket for temperature
18 control, a septum inlet and vent line, and a regulated supply of dry
19 ethylene and nitrogen, was dried and deoxygenated with a nitrogen
20 flow. 500 cc of dry, degassed hexane directly into the pressure
21 vessel 100 cc of purified 1,4-hexadiene was then charged into vessel
22 with a gas tight syringe. 10.0 cc of 0.785 molar (in total aluminum)
23 methyl alumoxane was injected into the vessel by a gas tight syringe
24 through the septum inlet and the mixture was stirred at 1,200 rpms
25 and 60°C for 5 minutes at 0 psig of nitrogen.

26 Bis(n-butyl-cyclopentadienyl)zirconium dichloride (1 mg) dissolved in
27 1.0 ml of dry, distilled toluene was injected through the septum
28 inlet into the vessel. After 1 minute, ethylene at 60 psig was
29 admitted and while the reaction vessel was maintained at 60°C. The
30 ethylene was passed into the vessel for 10 minutes at which time the
31 reaction was stopped by rapidly venting and cooling. 24.5 gms of
32 ethylene/hexadiene copolymer was recovered after evaporation of the
33 liquid component under nitrogen.

34 Example 1A

35 A 1-liter stainless steel pressure vessel, equipped with an
36 incline blade stirrer, an external water jacket for temperature
37 control, a septum inlet and vent line, and a regulated supply of dry

1 ethylene and nitrogen, was dried and deoxygenated with a nitrogen
2 flow. 500 cc of dry, degassed toluene and 100 cc of dry, degassed
3 1,4-hexadiene was injected directly into the pressure vessel. 10.0
4 cc of 0.785 molar (in total aluminum) methyl alumoxane solution in
5 toluene was injected into the vessel by a gas tight syringe through
6 the septum inlet and the mixture was stirred at 1,200 rpms and 70°C
7 for 5 minutes at 0 psig of nitrogen. Bis(n-butylcyclopenta-
8 dienyl)zirconium dichloride (0.10 mg) dissolved in 1.0 ml of dry,
9 distilled toluene was injected through the septum inlet into the
10 vessel. After 1 minute, ethylene at 50 psig was admitted and while
11 the reaction vessel was maintained at 70°C. The ethylene was passed
12 into the vessel for 30 minutes at which time the reaction was stopped
13 by rapidly venting and cooling. 9.6 gms of ethylene/1,4-hexadiene
14 copolymer was recovered after evaporation of the liquid components
15 under nitrogen.

16 Example 2

17 A 1-liter stainless steel pressure vessel, equipped with an
18 incline blade stirrer, an external water jacket for temperature
19 control, a septum inlet and vent line, and a regulated supply of dry
20 ethylene and nitrogen, was dried and deoxygenated with a nitrogen
21 flow. 500 cc of dry, degassed toluene, 50 cc of purified 1-hexene,
22 and 50 cc of dry, degassed 1,4-hexadiene were injected directly into
23 the pressure vessel. 10.0 cc of 0.785 molar (in total aluminum)
24 methyl alumoxane solution in toluene was injected into the vessel by
25 a gas tight syringe through the septum inlet and the mixture was
26 stirred at 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen.
27 Bis(n-butyl-cyclopentadienyl)zirconium dichloride (0.10 mg) dissolved
28 in 0.10 ml of dry, distilled toluene was injected through the septum
29 inlet into the vessel. After 1 minute, ethylene at 50 psig was
30 admitted and while the reaction vessel was maintained at 70°C. The
31 ethylene was passed into the vessel for 30 minutes at which time the
32 reaction was stopped by rapidly venting and cooling. 5.1 gms of
33 ethylene-1-hexene-1,4-hexadiene terpolymer was recovered after
34 evaporation of the liquid components under nitrogen.

35 Example 2A

36 A 1-liter stainless steel pressure vessel, equipped with an
37 incline blade stirrer, an external water jacket for temperature

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1 control, a septum inlet and vent line, and a regulated supply of dry
2 ethylene and nitrogen, was dried and deoxygenated with a nitrogen
3 flow. 500 cc of dry, degassed hexane was added directly into the
4 pressure flow. 100 cc of purified 4-vinylcyclohexene was charged
5 into reaction vessel with a gas tight syringe. 10.0 cc of 0.785
6 molar (in total aluminum) methyl alumoxane solution in toluene was
7 injected into the vessel by a gas tight syringe through the septum
8 inlet and the mixture was stirred at 1,200 rpms and 70°C for 5
9 minutes at 0 psig of nitrogen.

10 Bis(n-butyl-cyclopentadienyl)zirconium dichloride (0.1 mg) dissolved
11 in 1.0 ml of dry, distilled toluene was injected through the septum
12 inlet into the vessel. After 1 minute, ethylene at 62 psig was
13 admitted and while the reaction vessel was maintained at 60°C. The
14 ethylene was passed into the vessel for 10 minutes at which time the
15 reaction was stopped by rapidly venting and cooling. 25.6 gms of
16 ethylene/4-vinyl cyclohexene copolymer polyethylene was recovered
17 after evaporation of the liquid components under nitrogen.

18 Example 2B

19 A 1-liter stainless steel pressure vessel, equipped with an
20 incline blade stirrer, an external water jacket for temperature
21 control, a septum inlet and vent line, and a regulated supply of dry
22 ethylene and nitrogen, was dried and deoxygenated with a nitrogen
23 flow. 250 cc of dry, degassed toluene and 200 cc of purified
24 4-vinylcyclohexene were injected directly into the pressure vessel.
25 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane in
26 toluene solution in toluene was injected into the vessel by a gas
27 tight syringe through the septum inlet and the mixture was stirred at
28 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen.

29 Bis(n-butylcyclopentadienyl)zirconium dichloride (0.05 mg) dissolved
30 in 0.050 ml of dry, distilled toluene was injected through the septum
31 inlet into the vessel. After 1 minute, ethylene at 25 psig was
32 admitted and while the reaction vessel was maintained at 70°C. The
33 ethylene was passed into the vessel for 3 minutes at which time the
34 reaction was stopped by rapidly venting and cooling. 7.3 gms of
35 ethylene/4-vinylcyclohexene copolymer was recovered after evaporation
36 of the liquid components under nitrogen.

37 The structural properties of the polymers of the Examples

- 1 are reflected in the drawing figures and reported in the following
- 2 Table. Data on commercial polymers are reported in the Table and
- 3 displayed in the drawing figures for comparison.

TABLE

RESIN	COMONOMER CONTENT (MOLE PERCENT)				M_w ($\times 10^3$)	M_w/M_n	COMPOSITION DISTRIBUTION	CLUSTER INDEX	MELTING BEHAVIOUR	
	TYPE	AMOUNT	TYPE	AMOUNT					DISTRIBUTION	PEAK M.P. ($^{\circ}$ C)
EXAMPLE 1	1,4 HEXADIENE	2.3	-	-	70.5	1.75	NARROW	5.0	NARROW	111.9
EXAMPLE 2	1,4 HEXADIENE	2.0	HEXENE-1	1.9	62.6	1.80	-	-1	NARROW	101.0
EXAMPLE 2A	4-VINYLCYCLO- HEXENE	0.4	-	-	95.3	1.87	NARROW	-	NARROW	120.5
3 - EXXON LL 3001	HEXENE-1	3.7	-	-	103.1	3.30	BROAD	12.1	BROAD	124.6
4 - DOWLOX 2045	OCTENE-1	2.8	-	-	114.6	3.67	BROAD	9.5	BROAD	124.3
5 - EXXON LL 1001	BUTENE-1	4.4	-	-	118.0	3.33	BROAD	11.7	BROAD	121.6
6 - DUPONT SCLAIR 110	BUTENE-1	3.3	-	-	115.7	3.79	BROAD	5.0	BROAD	118.7
7 - MITSUI 2020L	4-METHYL- PENTENE-1	3.5	-	-	92.3	2.6	BROAD	-	BROAD	124.5
8 - LLDPE2	BUTENE-1	5.2	-	-	96.1	1.78	NARROW	9.6	NARROW	94.0

1. ANALYZED BUT ONLY LOW QUALITY SPECTRA OBTAINED - IMPRECISE RESULT.
2. LABORATORY PREPARATION WITH A SOLUBLE VANADIUM OXYCHLORIDE/ETHYL ALUMINUM SESQUICHLORIDE CATALYST.

CLAIMS:

1. A copolymer composition from the polymerization of ethylene and at least one comonomer comprising an alpha, internal nonconjugated diene, said copolymer composition having incorporated in its structure at least 3 mole percent of units of said at least one comonomer, said copolymer composition having a cluster index of about 9 or less, and said copolymer composition having an alpha-olefin content less than 15 weight percent.
2. The copolymer composition of claim 1 having a molecular weight distribution of about 3.0 or less.
3. The copolymer composition of claim 2 having a molecular weight distribution of about 2.5 or less.
4. The copolymer composition of claim 3 having a molecular weight distribution of about 2.0.
5. The copolymer composition of claim 1 having a comonomer composition distribution wherein more than 55 weight percent of the copolymer is within 50 percent of the median comonomer content in mole percent, of said composition.
6. The copolymer composition of claim 5 having greater than 55 weight percent of the copolymers within 50 percent of the median comonomer content in mole percent.
7. A copolymer composition of claim 1 having a cluster index of about 7 or less.
8. A copolymer composition of claim 7 having a cluster index of about 5 or less.
9. The copolymer composition of claim 1 having a monomer composition comprising about 0.1-25 mole percent of said diene.

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10. The copolymer composition of claim 9 having a monomer composition comprising about 0.1-10 mole percent of said diene.

11. The copolymer composition of claim 9 having a monomer composition comprising 0.1-2 mole percent of said diene.

12. The copolymer composition of claim 1 wherein said copolymer is an interpolymer comprising ethylene, said diene, and at least one other polymerizable unsaturated comonomer.

13. The copolymer composition of claim 1 wherein said at least one other polymerizable unsaturated comonomer is an alpha-olefin.

14. The copolymer composition of claim 1 wherein said alpha-olefin is propylene, butene-1, or hexene-1.

15. The copolymer composition of claim 1 having a density of about 0.85-1.0.

16. The copolymer composition of claim 15 having a density of about 0.87-0.90.

17. The copolymer composition of claim 15 having a density of about 0.90-0.915.

18. The copolymer composition of claim 15 having a density of about 0.915-0.940.

19. The copolymer composition of claim 15 having a density of about 0.940-0.960.

20. The copolymer composition of claim 2 having a comonomer composition distribution wherein greater than 55 weight percent of the copolymer is within 50 percent of the median comonomer content in mole percent.

21. The copolymer composition of claim 1 wherein said copolymer has incorporated in its structure at least 5 mole percent of units of said at least one comonomer.

22. The copolymer composition of claim 1 wherein said at least 5 mole percent units of said at least one comonomer includes at least about 0.01 mole percent of units of said diene.

23. The copolymer composition of claim 22 containing at least about 0.1 mole percent units of said diene.

24. The copolymer composition of claim 23 containing at least about 1 mole percent units of said diene.

25. The copolymer composition of claim 24 containing at least about 3 mole percent units of said diene.

26. The copolymer composition of claim 25 containing at least 5 mole percent units of said diene.

27. The copolymer composition of claim 1 wherein said at least 3 mole percent units of said at least one comonomer consist essentially of said diene.

28. The copolymer composition of claim 1 wherein said diene is a linear diene.

29. The copolymer composition of claim 28 wherein said linear diene is a 1,4-hexadiene, substituted or unsubstituted.

30. The copolymer composition of claim 29 wherein said diene is 1,4-hexadiene.

31. The copolymer composition of claim 1 wherein said diene is a cyclic diene.

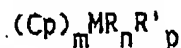
- 31 -

32. The copolymer composition of claim 1 wherein said cyclic diene is 4-vinylcyclohexene.

33. The copolymer composition of claim 27 wherein said diene is 1,4-hexadiene.

34. A copolymer composition of ethylene and an alpha, internal nonconjugated diene (diolefin) having a cluster index of about 9 or less, a molecular weight distribution of about 3.0 or less, a comonomer composition distribution of more than 55 weight percent of the copolymer within 50 percent of the median comonomer content in mole percent, said copolymer being formed by polymerization in the presence of a catalyst system comprising a metallocene of a metal of Group IVB, VB, and VIB of the Periodic Table and an alumoxane or a reaction product thereof, and said copolymer composition having an alpha-olefin content less than 15 weight percent.

35. The copolymer composition of claim 34 wherein the catalyst system metallocene is represented by



wherein Cp is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IVB, VB, or VIB transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl group having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M.

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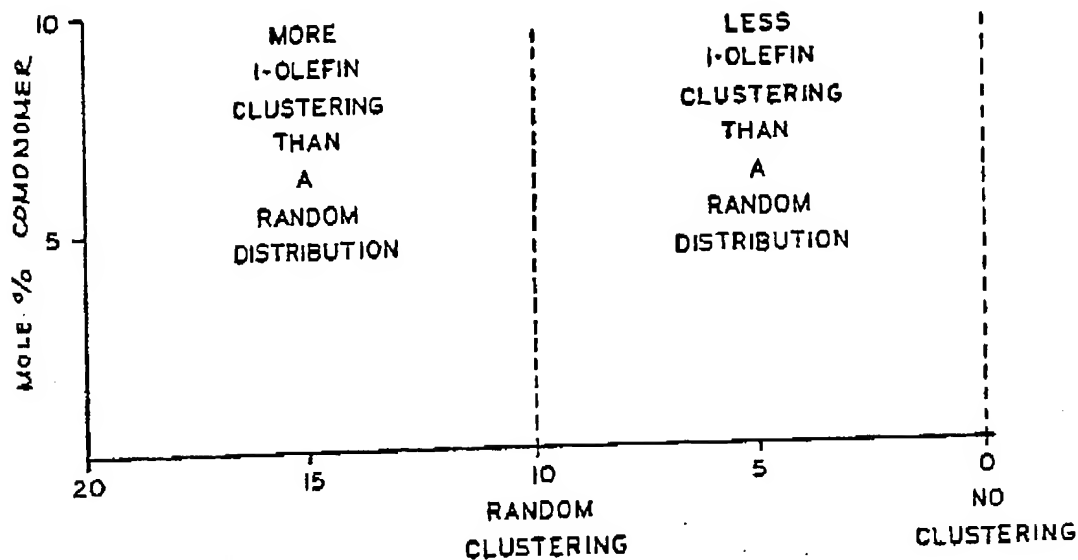


FIG.1

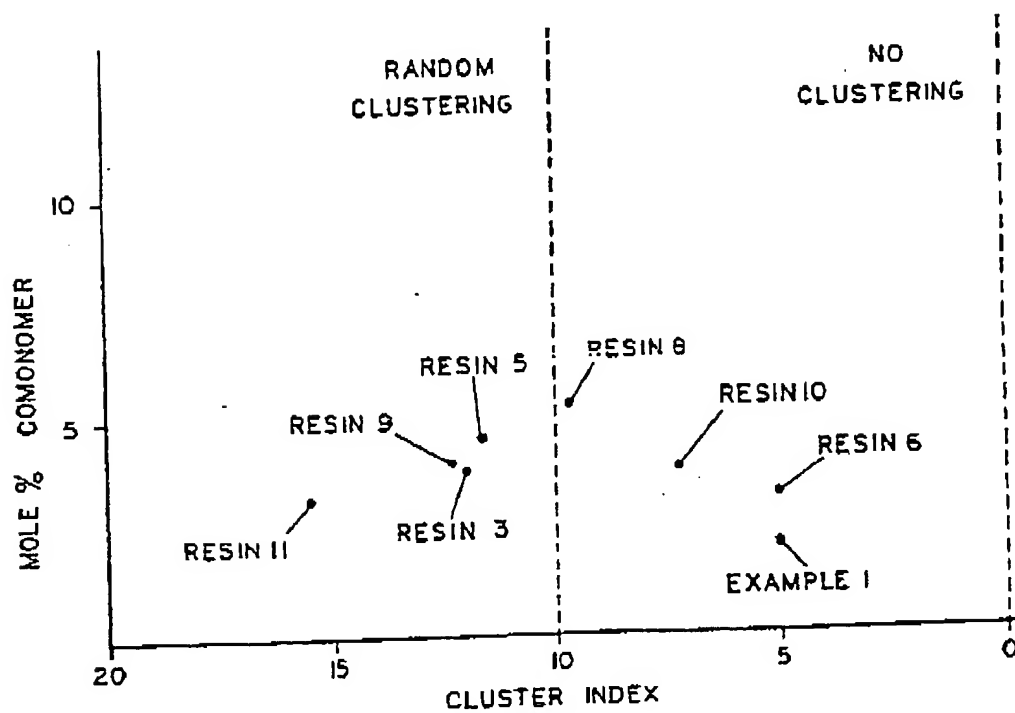
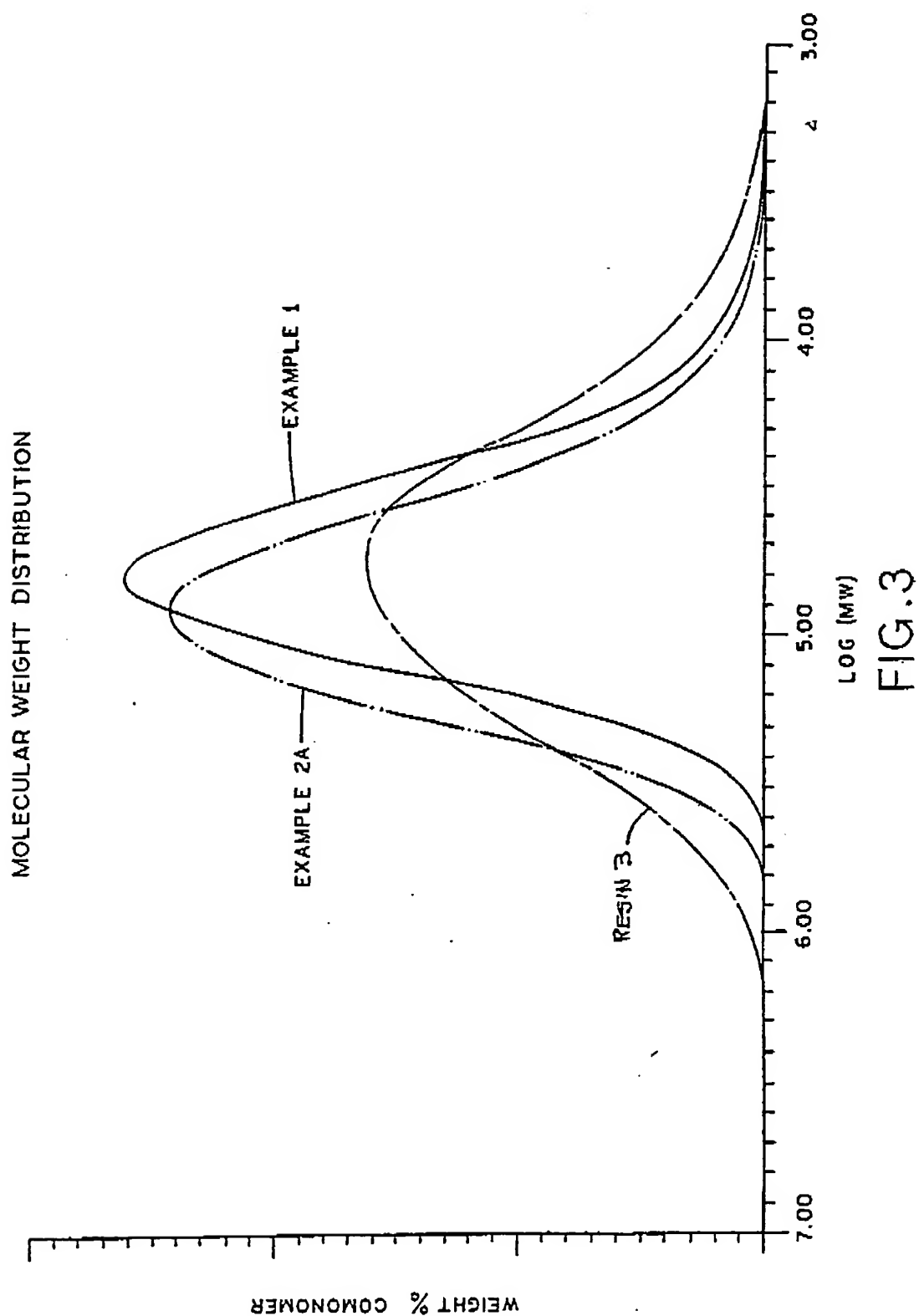
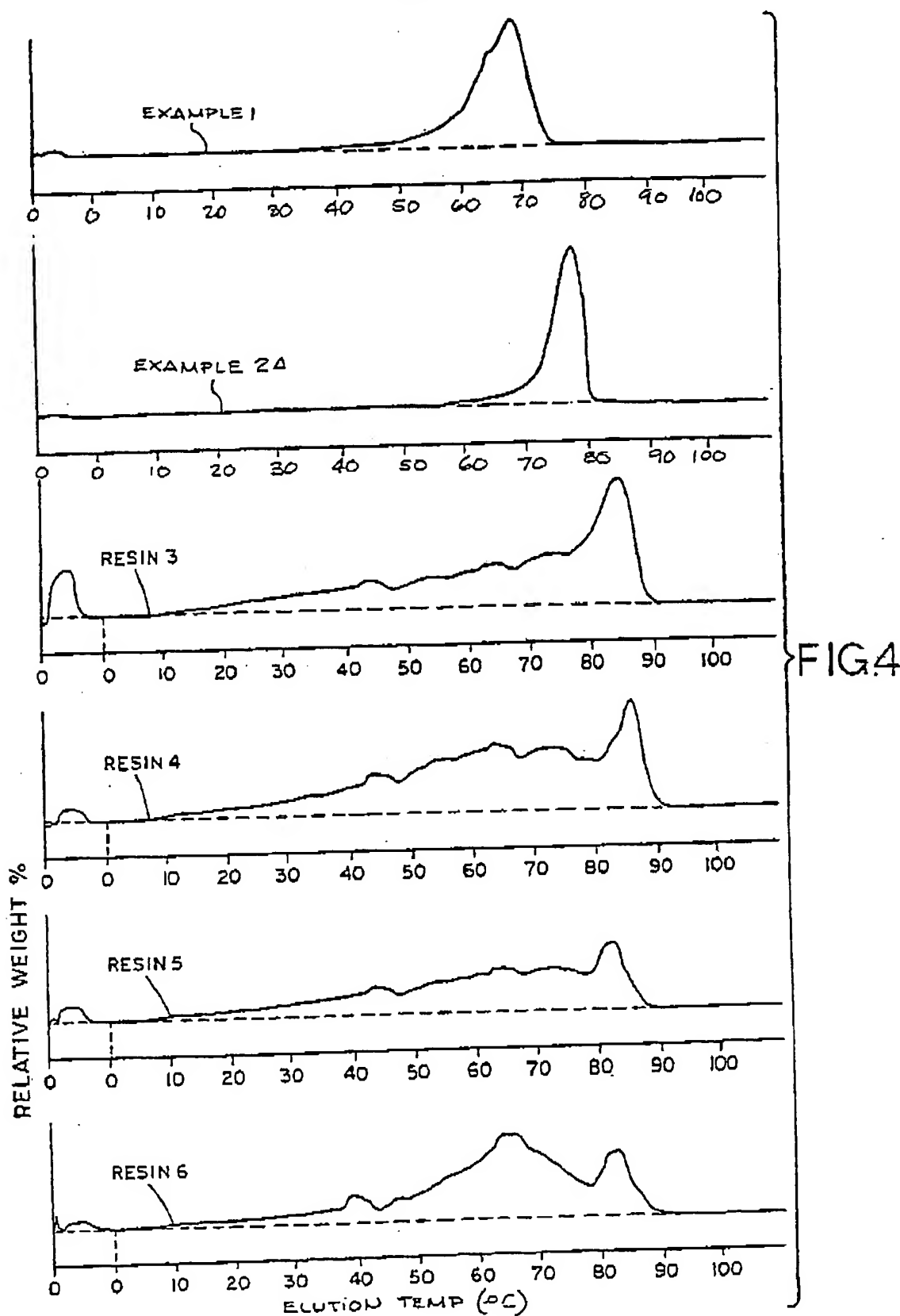


FIG.2



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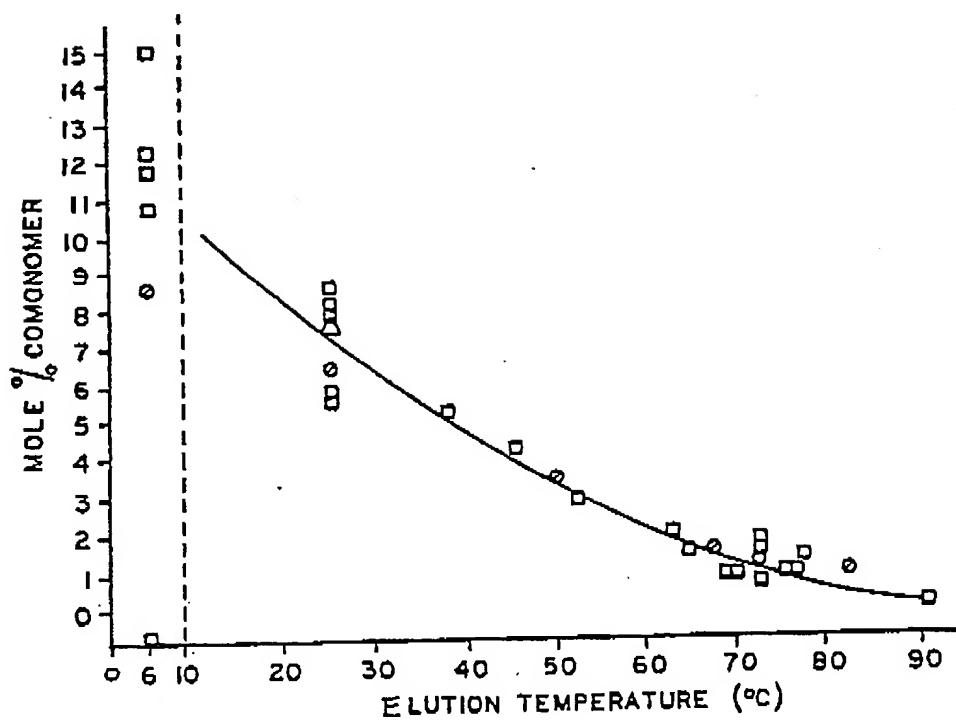


FIG. 5

BUTENE	COMONOMER	○
HEXENE	COMONOMER	□
OCTENE	COMONOMER	△

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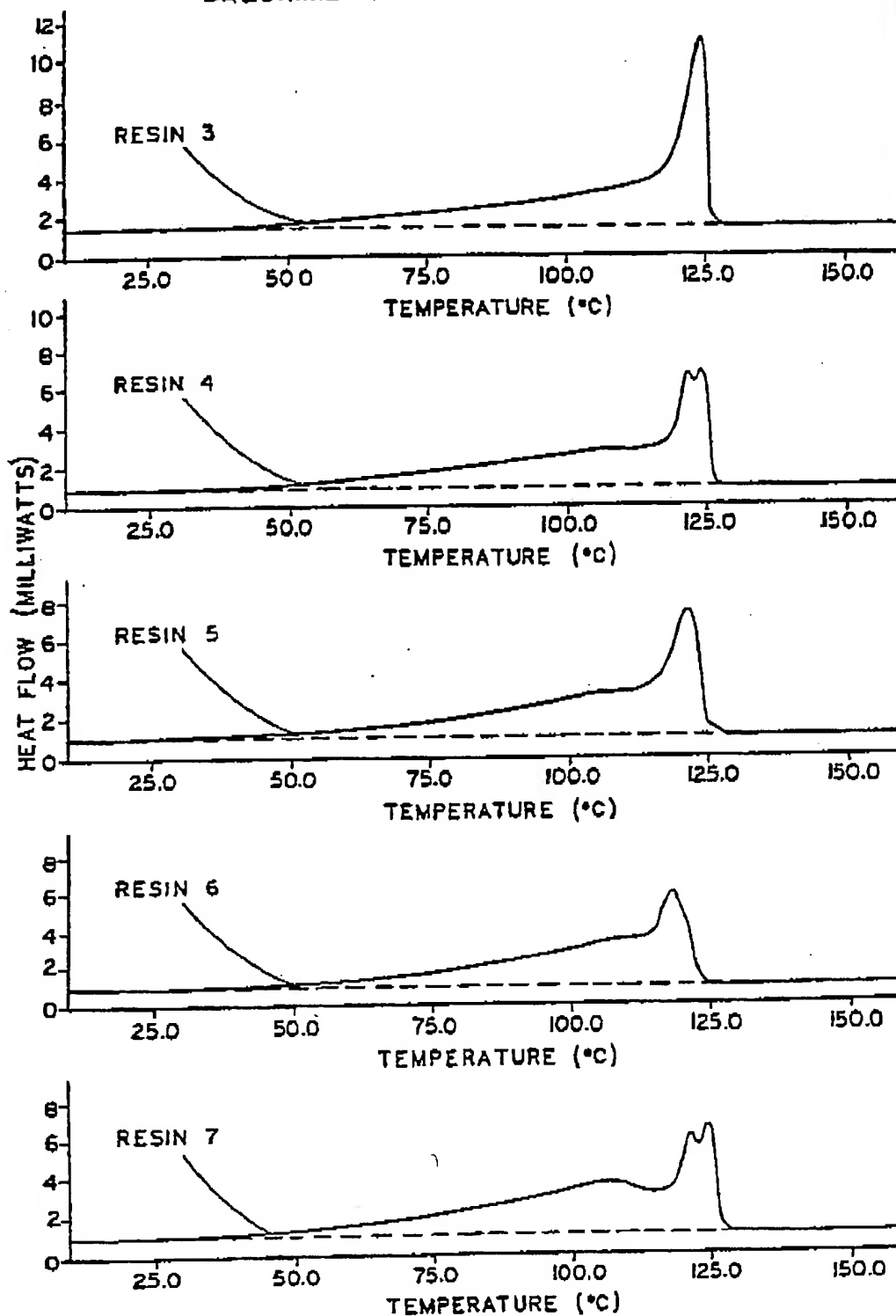
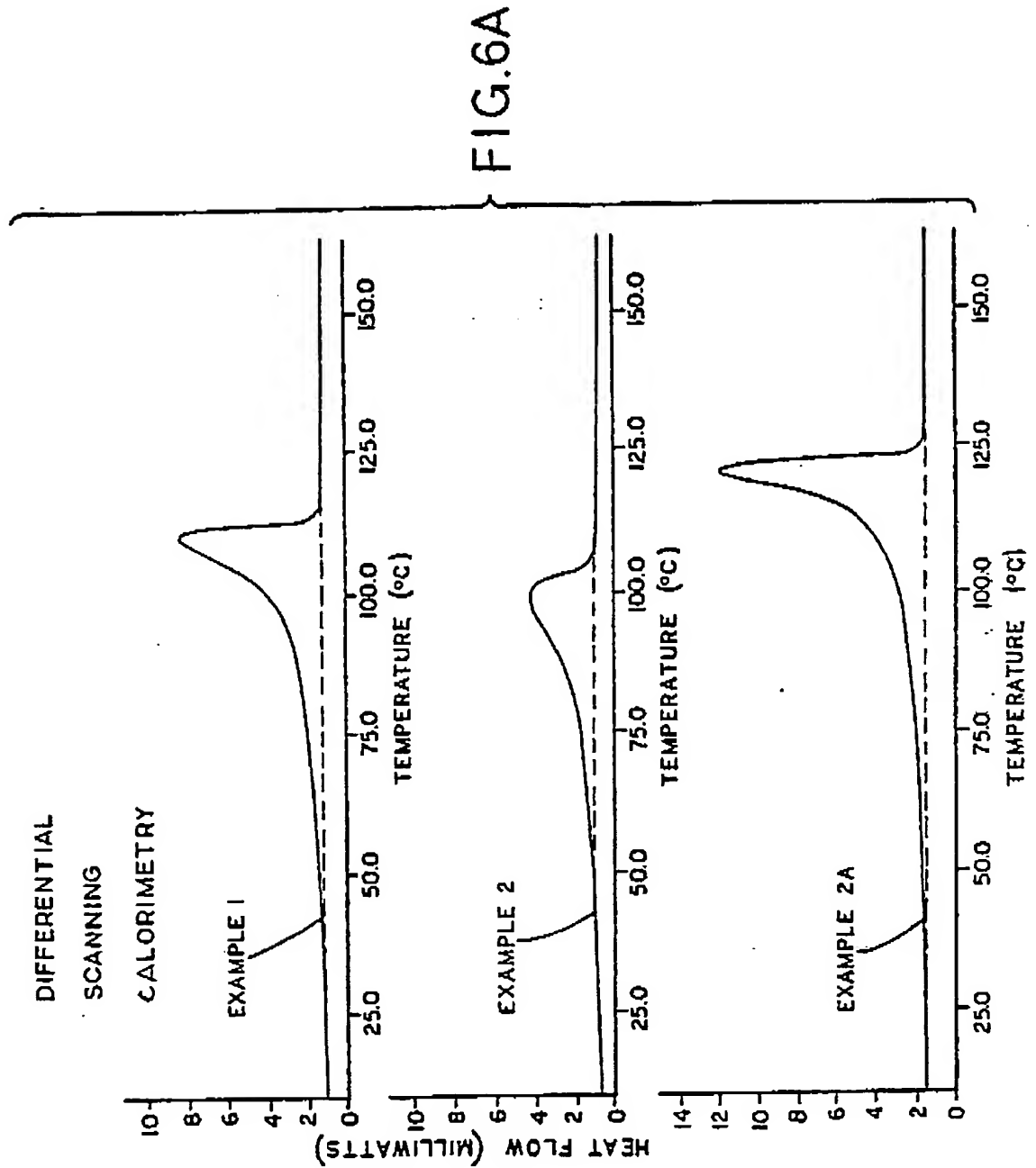
DIFFERENTIAL
SCANNING
CALORIMETRY

FIG.6



INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 87/03299**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 210/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0069951 (HOECHST) 19 January 1983 see claims 1-8 --	1
A	US, A, 4306041 (C. COZEWITH) 15 December 1981 see claims 1-19; column 3, lines 34-56 --	1
A	GB, A, 2099836 (MONTEDISON) 15 December 1982 see claims 1-7 --	1
P,X	EP, A, 0223394 (UNIROYAL CHEMICAL) 27 May 1987 see claims 1-17; page 3, line 42 - page 5, line 15 -----	1-35
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15th April 1988	02 JUN 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8703299
SA 20109

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		US-A- 4542199	17-09-85
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		FR-A- 2507189	10-12-82
		JP-A- 58002310	07-01-83
		NL-A- 8202251	03-01-83
		DE-A- 3221853	17-02-83
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		JP-A- 62095304	01-05-87
		US-A- 4668834	26-05-87

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82